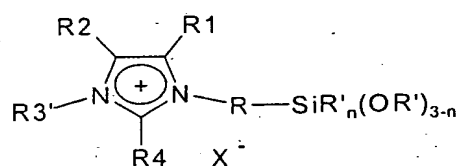
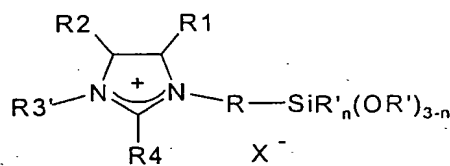


PATENT CLAIMS

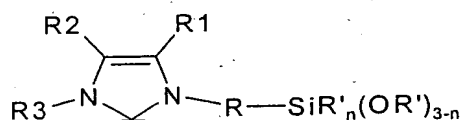
1. Process for the immobilisation of N,N-disubstituted imidazolium salts, N-heterocyclic carbene ligands and ruthenium catalysts containing N-heterocyclic carbene ligands on inorganic oxide supports, characterised in that a compound of the general formula (I), (II), (III), (IV), (V) or (VI)



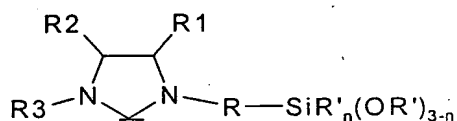
(I)



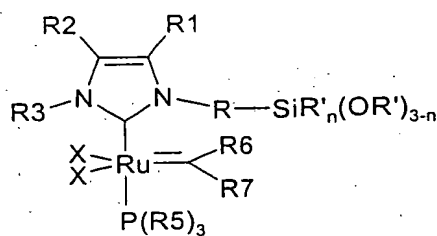
(II)



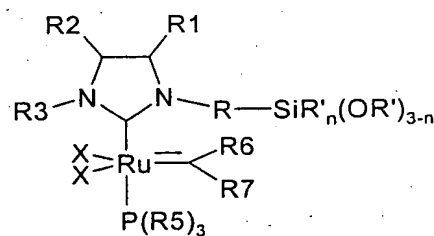
(III)



(IV)



(V)



(VI)

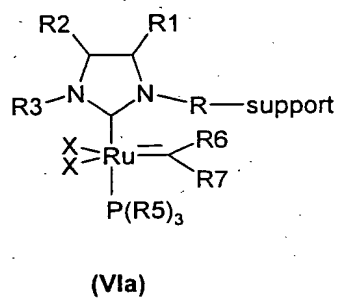
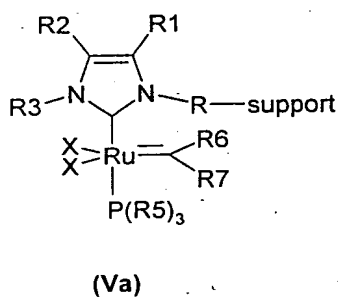
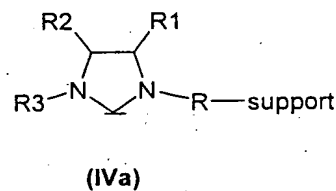
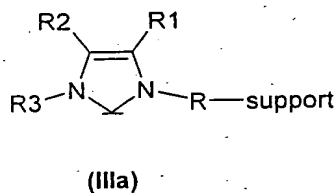
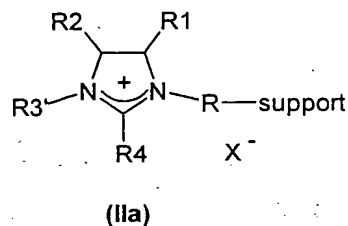
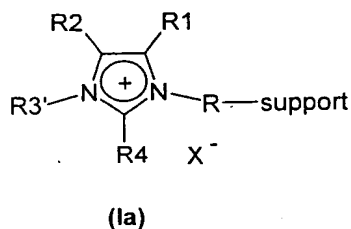
in which

R is A, Ar, A-Ar, A-Ar-A, Het, AHet or AHetA having a total of not more than 30 carbon atoms, where

A is a straight-chain, branched or saturated C₁-C₂₀-alkyl radical, cycloalkyl or cycloalkyl bonded via one or two alkyl group(s) having a total of 4 – 30 carbon atoms, where one CH₂ or CH

group both in the alkyl radical and in the cycloalkyl radical may be replaced by N, NH, NA, O and/or S and H atoms may be replaced by OA, NA₂ and/or PA₂,

- 5 Ar is a mono- or polysubstituted or unsubstituted aromatic hydrocarbon having a total of not more than 20 carbon atoms, where substituents may be A, Hal, OA, NA₂, PA₂, COOA, COA, CN, CONHA, NO₂, =NH or =O,
- 10 Het is a monocyclic or bicyclic, saturated or aromatic heterocyclic radical having from 1 to 4 N, O and/or S atoms, which may be unsubstituted or mono-, di- or trisubstituted by Hal and/or A, OA, COOA, COA, CN, CONHA, NA₂, PA₂, NO₂, =NH or =O, where
- Hal is F, Cl, Br or I,
- R', independently of the position in the molecule, is A or Ar having 1 – 12 carbon atoms,
- 15 R3 is A, Ar, AAr, AArA, Het, AHet or AHetA having 6 – 18 carbon atoms,
- R3' is straight-chain or branched cycloalkyl or cycloalkyl bonded via one or two alkyl group(s), Ar, AAr, AArA, Het, AHet or AHetA having a total of 4 – 30 carbon atoms,
- 20 R1 and R2, independently of one another, are H, Cl, Br or are as defined for R3,
- R4 is H, Cl, Br or a straight-chain, branched, saturated or mono- or polyunsaturated C₁-C₇-alkyl radical, where one or more H in the alkyl radical may be replaced by Z,
- 25 R5 is A, Ar or AAr,
- R6 and R7 are H, A or Ar, where H atoms in A or Ar may be substituted by alkenyl or alkynyl radicals,
- X are anionic ligands which are identical to or different from one another, and
- 30 n is 0, 1 or 2,
- is reacted with an inorganic metal oxide containing active OH groups on the surface, in an anhydrous, inert, aprotic, organic solvent with formation of an alcohol R'OH under a protective-gas atmosphere, the product (Ia), (IIa), (IIIa), (IVa), (Va) or (VIa)



20 in which R, R1, R2, R3, R3', R4, R5, R6, R7 and X are as defined above, and "-support" denotes an inorganic oxide, is separated off and, if necessary, purified.

- 25 2. Process according to Claim 1, characterised in that the protective-gas atmosphere used is nitrogen or argon.
- 30 3. Process according to Claim 1, characterised in that the product formed is separated off by filtration and, if necessary, purified by washing with a suitable solvent.
- 35 4. Process according to Claim 1, characterised in that it is carried out by the batch method.
5. Process according to Claim 1, characterised in that it is carried out by a continuous method.

- 5 6. Process according to one or more of Claims 1 – 5, characterised in that the inorganic oxides used are natural or chemically prepared particulate or monolithic oxides of silicon, boron, aluminium, titanium and zirconium or mixed oxides thereof, or zeolites.
7. Process according to one or more of Claims 1 – 5, characterised in that the inorganic oxides used are particulate or monolithic oxides of silicon or aluminium or mixed oxides thereof.
- 10 8. Process according to one or more of Claims 1 – 5, characterised in that the inorganic oxides used are particulate or monolithic oxides of silicon, which can be a silica gel or naturally occurring silicate derived from chain-, ribbon- and layer-form silicic acids.
- 15 9. Process according to one or more of Claims 1 – 5, characterised in that the solvents used are hydrocarbons, halogenated hydrocarbons or cyclic ethers.
- 20 10. Process according to one or more of Claims 1 – 5, characterised in that the solvents used are pentane, hexane, heptane, octane, decane, benzene, toluene, methylene chloride, chlorobenzene, trichlorotoluene, tetrahydrofuran or mixtures thereof.
- 25 11. Process according to one or more of Claims 1 – 5, characterised in that the starting compounds of the general formulae (I) to (VI) are added in a 0.01 – 100-fold excess with respect to the active OH groups on the oxide surface, preferably in a 0.1 – 50-fold excess and very particularly preferably in a 0.5 – 10-fold excess.
- 30 12. Process according to one or more of Claims 1 – 5, characterised in that the reaction is carried out at a temperature in a range between -20°C and +150°C, preferably between 0°C and +120°C, within a reaction time of from 30 minutes to 10 days, preferably from one hour to 2 days and very preferably from one hour to one day.

13. Process according to one or more of Claims 1 – 5, characterised in that, when the reaction is complete, the products (Ia) to (VIa) formed are separated off by filtration, optionally washed with a solvent selected from the group consisting of pentane, hexane, heptane, octane, decane, benzene, toluene, methylene chloride, chlorobenzene, trichlorotoluene and tetrahydrofuran or mixtures thereof, and subsequently dried.
14. Process according to one or more of Claims 1, 3 and 5, characterised in that solutions of the compounds of the general formulae (I) to (VI) are pumped continuously through the monolithic material, where the monolith is set to a temperature between -20°C and +150°C, and the functionalised monolith is washed, when the reaction is complete, with a solvent selected from the group consisting of pentane, hexane, heptane, octane, decane, benzene, toluene, methylene chloride, chlorobenzene, trichlorotoluene and tetrahydrofuran or mixtures thereof.
15. Process according to Claim 14, characterised in that solutions of the compounds of the general formulae (I) to (VI) are circulated continuously by pump, causing repeated flow through the monolith.
16. Process according to one or more of Claims 1 – 4, characterised in that the inorganic oxides are mixed and brought to reaction with the solutions of the compounds of the general formulae (I) to (VI).
17. N,N-disubstituted imidazolium salts of the general formulae (Ia) and (IIa), N-heterocyclic carbene ligands of the general formulae (IIIa) and (IVa) and ruthenium catalysts containing N-heterocyclic carbene ligands of the general formulae (Va) and (VIa) immobilised on inorganic oxide supports.
18. Use of the compounds of the general formulae (Ia) and (IIa) as immobilised reaction media, immobilised ionic fluids, immobilised ligand or catalyst precursors and as immobilised catalysts in organic, organometallic and transition metal-catalysed syntheses.

19. Use of the compounds of the general formulae (IIIa) and (IVa) as starting materials for the preparation of immobilised N-heterocyclic carbene-metal complexes.
- 5 20. Use of the compounds of the general formulae (IIIa) and (IVa) as immobilised ligands in catalytic reactions, in particular in ruthenium-catalysed metathesis reactions, palladium-catalysed Heck or Suzuki reactions, rhodium-catalysed hydrogenations, furan syntheses, hydroformylations, isomerisations or hydrosilylations.
- 10 21. Use of the compounds of the general formulae (Va) and (VIa) as immobilised catalysts in organic and organometallic synthesis.
- 15 22. Use of the compounds of the general formulae (Va) and (VIa) as catalysts in C-C coupling reactions, hydrogenations, isomerisations, silylations and hydroformylations.
- 20 23. Use of the compounds of the general formulae (Va) and (VIa) as immobilised catalysts for C-C coupling reactions, such as olefin metathesis, and for hydrogenation reactions, olefin metathesis reactions, such as cross metathesis (CM), ring closure metathesis (RCM), ring opening metathesis polymerisation (ROMP), acyclic diene metathesis polymerisation (ADMET) and ene-yne metathesis.

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